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Tannin-based flax fibre reinforced composites for structural applications in vehicles

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Abstract. Innovation is often driven by changes in government policies regulating the industries, especially true in case of the automotive. Except weight savings, the strict EU regulation of 95% recyclable material-made vehicles drives the manufactures and scientists to seek new 'green materials' for structural applications. With handing at two major drawbacks (production cost and safety), ECHOSHELL is supported by EU to develop and optimise structural solutions for superlight electric vehicles by using bio-composites made of high-performance natural fibres and resins, providing enhanced strength and bio-degradability characteristics. Flax reinforced tannin-based composite is selected as one of the candidates and were firstly investigated with different fabric lay-up angles (non-woven flax mat, UD, $[0, 90°]_4$ and $[0, +45°, 90°, -45°]_2$) through authors' work. Some of the obtained results, such as tensile properties and SEM micrographs were shown in this conference paper. The UD flax reinforced composite exhibits the best tensile performance, with tensile strength and modulus of 150 MPa and 9.6 MPa, respectively. It was observed that during tension the oriented-fabric composites showed some delamination process, which are expected to be eliminated through surface treatment (alkali treatment etc.) and nanotechnology, such as the use of nano-fibrils. Failure mechanism of the tested samples were identified through SEM results, indicating that the combination of fibre pull-out, fibre breakage and brittle resins failure mainly contribute to the fracture failure of composites.

1. Introduction

To meet the current EU recyclability regulation in vehicle industries, one of the important achievements is the investigation and usage of natural composites, also called bio-composites which provide potential good mechanical performances and outstanding environmental advantages. The ECOSHELL project concentrates on the use of sustainable technologies and lays emphasis on the use of flax/tannin composites for structural applications in superlight vehicles. There is a gap found in literature in this area and more research at fundamental level needs to be done.

To date, tannin resins extracted from plants are widely used and reported as adhesives, however, there are still a small number of papers about tannin matrix composites. Coir fibre-reinforced tannin composites were firstly studied by Vilmar et al. [1] to show a potential for automotive applications as internal parts. Ndazi and his co-workers [2] also manufactured composite panel boards from rice husks and mimosa tannin resins. The interest of studying tannin-based composites has been increasing very fast due to some advantages: (i) non-toxic; (ii) wide availability; (iii) fast curing rate.

Many studies [3] concentrated on flax composites and provided valuable information, some of which is exhibited in **Table 1**. From Van de Velde and Kiekens [3] investigations, polypropylene (PP) is the most suitable thermoplastic matrix for a flax-reinforced composite due to its extraordinary advantages, such as low density, low thermal expansion, good resistance to water and recyclability. Compared to the thermoplastic-based bio-composites, thermoset composites coming from vegetable oils (e.g. soybean oil and linseed oil) are preferred in the structure applications [4]. Akesson et al. [5] produced and studied thermoset composites from Lactic Acid-based (LA) resins and flax fibres. LA resin, a polyester resin containing carbon-carbon bonds, was cured at elevated temperature, together with impregnated flax fibres during compression moulding; the mechanical properties of final composites were increased by varying the fibre content from 40 wt% to 70 wt%, but drastically reduced with a fibre ratio of 75 wt%. Hughes et al. [6] also produced unsaturated polyester resin composites reinforced by unidirectional flax fibres and directed their investigation towards the tensile deformation behaviour. As an example of characterization of physical properties, the storage modulus of LA composites reinforced with 70 wt% flax fibres is 9.32 GPa and 3.29 GPa at 20 °C and 140 °C, respectively [5]. SEM is also an important characterisation method for composite technology (e.g. failure mechanism) and thus widely reported in the literature [7].

Table 1. Collected mechanical properties of flax reinforced composites.

Fibre/ Matrix	Processing	Tensile strength	Tensile modulus	Flexural Strength	Reference
Flax/bio-thermoset (MSO[a])	Compression moulding	50-120 MPa	6-15 GPa	180 MPa (max)	[8]
Flax/bio-thermoset (MMSO[b])	Compression moulding	50-120 MPa	7-15 GPa	201 MPa (max)	[8]
Arctic Flax/Epoxy (50:50)	Resin transfer moulding	280 MPa	40 GPa		[9]
Plain-woven flax/ thermoset	Compression Moulding	280 MPa	32 GPa	250 MPa	[10]
Flax yarn/ SPC[c] resins	Pultrusion	298 MPa	4.3 GPa	117 MPa	[11]
Flax/Lactic acid resins(70:30)	Compression moulding	62 MPa	9 GPa	96 MPa	[5]
Flax/ PLA (polyactic acid)	Injection moulding	40-55 MPa	3-6 GPa		[12]

*a-Methacrylated soybean oil, b-methacrylic anhydride-modified soybean oil, c-Soy Protein Concentrate Resin.

Concerning with the incompatibility between polymer matrix (hydrophobic) and flax fibres (hydrophilic), surface treatment and nanotechnology are used to handle at the issue and hence improve the whole composite performance. Alkali treatment, esterification and silane treatment are common surface treatment on flax fibres to improve the flax/polymer surface adhesion [13; 14]. Compared to the traditional produced flax fibres containing amorphous materials, nano-flax fibres provide high crystallinity by removing hierarchical structure and show a high crystal stiffness [15]. The significant enhancements of nano-flax fibre-reinforced composites are dispersion, thermal and mechanical properties due to high aspect ratio (length/diameter), resulting in the formation of rigid filler network [16-18]. Seydibeyoglu and his coworkers [17] demonstrated that the 16.5% cellulose nanofibrils reinforced polyurethane composites not only show highest strength increase of 500% but also have a stable storage modulus even at low temperature of -31°C. Nano-fibrillate flax fibres from high pressure disintegration have been reported to show good homogeneous dispersion and enhanced mechanical properties in polyvinyl alcohol matrix [18] .

Due to the inherent environmental benefits of using natural resin (tannin) and natural fibres (flax), it was decided to put this new composite technology to use. From the literature research, this new composite is only reported by Pizzi et al. [19] who manufactured the mimosa tannin-based composites reinforced by non-woven mat of flax fibres and also studied their mechanical properties. We clearly find a big knowledge gap in the mechanical/physical properties of flax/tannin composite, together with the environmental aging problems (temperature, humidity etc.) A methodology was developed to

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systematically analyse and characterise the properties of the composite in various parameters like fibre fabric arrangements.

2. Experimental

2.1. Materials

The flax mat/tannin composites were provided by ENSTIB. Other samples with various fabric orientations were supplied by MaHyTec. The details of the materials are shown in **Table 2**. The sample size for different characterizations was discussed in following methodology chapter.

Table 2. Flax/tannin composite systems supplied by manufacturers.

Type	Fabric form	Supplier	Manufacturing
A	Flax mat	ENSTIB	Compression moulding
B	UD (8 plies)	MaHyTec	Compression moulding
C	$[0, 90°]_4$	MaHyTec	Compression moulding
D	$[0, +45°, 90°, -45°]_2$	MaHyTec	Compression moulding

2.2. Tensile test of composite

The flat coupon tensile test was carried out on the Instron 50/100 kN machine according to ASTM D3039 at the cross head speed of 2mm/min. The test specimens were cut by the suppliers and received with a size of 250×25mm2. The average thickness was 2.5 mm. To obtain micro-scale elongation information during test, digital image correlation (DIC) method, together with a placed extensometer, was used on each specimen (see **Figure 1**). Three specimens were tested at room temperature for every composite type, and the average modulus and strength were obtained.

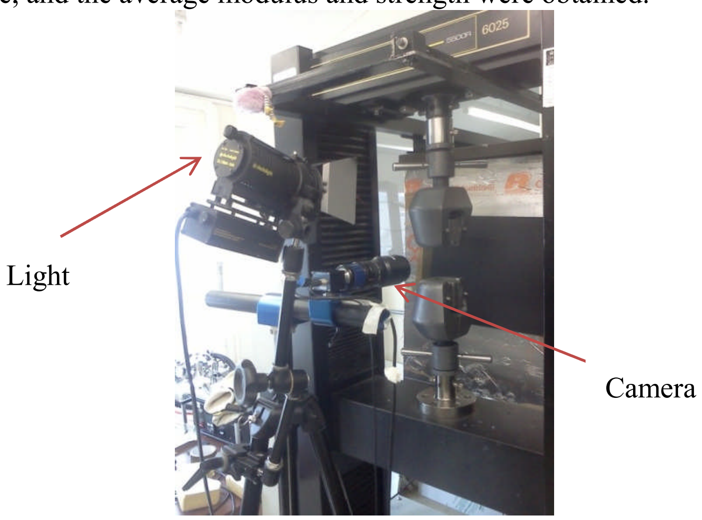

Figure 1. DIC technique applied to provide micro-scale information.

2.3. Scanning electron microscopy

Cross-section surface topographies of the composites after tensile testing were examined using a XL30 SFEG analytical high resolution scanning electron microscopy (SEM), supplied by FEI. Prior to SEM investigation, the test specimens were vacuum –coated with thin layers of gold powder to avoid the electrical charging during analysis. The whole examination was carried out at room temperature. Micrographs of surfaces were produced at various magnifications.

3. Results and Discussion

3.1. Tensile properties of composites

Both macro and micro-scale information of tensile properties were obtained through the experiments. Tensile strength, maximum strain, tensile modulus were easily read from the micro-scale stress-strain curve, while the macro-scale load-elongation curves to some extent explain the macro-mechanism of failure, which was also roughly shown through the SEM micrographs.

Using DIC to reduce the factor of dimension change under stress and offer advantages of non-contact, **Figure 2**(a) shows the relationship between stress and strain at micro-scale level obtained through the DIC method. Theoretically, the stress-strain curves measured by DIC were non-linearand thus the quantitative values were plotted as scatter diagrams. UD flax fabric/tannin samples have the best tensile strength up to 150 MPa, which is very competitive to some results in the literature [5, 8], due to the unidirectional fabric form significantly improving the tensile properties in their longitudinal direction. The [0, +45°, 90°,-45°]$_2$ composite were found to have less tensile strength but larger maximum strain than the [0, 90°]$_4$ type. This indicates that samples with [0, 90°]$_4$ fabric orientation are more brittle. The tensile strength and maximum strain of flax mat/mimosa tannin composites (type A) reaches the lowest values of 55 MPa and 0.7%, respectively, which is attributed to the random distribution of flax fibres.

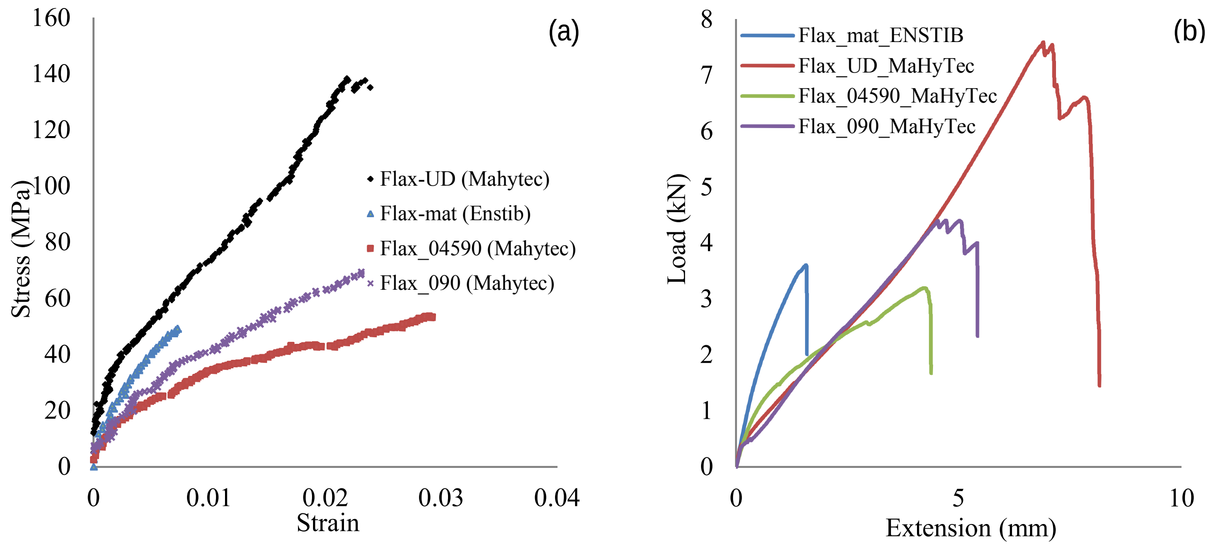

Figure 2. (a) micro-scale stress-strain curve; (b) macro-scale load-elongation curve.

Figure 3 represents the tensile modulus measured as the tangent modulus in the initial linear portion in the stress-strain curves. The portion close to zero point is not acceptable as a result of machine calibration. The young's modulus of specimen follows the trend B>C>D. Similar to tensile strength, the unidirectional fibres in type B apparently give rise to the maximum composite young's modulus of approximately 9.6 GPa. The [0, 90°]$_4$ layer arrangement (type C) produces higher Young's modulus of 4.8 GPa than the [0, 45°, 90°,-45°]$_2$ composite (type D), in accordance with tensile strength. One thing noticed is that the flax mat reinforced tannin composites (type B) shows a second highest value of Young's modulus (6.4 GPa), which is not compatible with the values of other types due to the different manufacturing details.

The failure mechanism can be indicated from **Figure 2**(b), illustrating the macro-scale load-extension curves for different tannin composites. After the maximum force, the loads applied on the flax mat composite (type A) dropped down immediately, whereas other three composite types behave in a different way (z-curves in **Figure 2**(b)). The first peak of composite B may be due to the combination of failure of tannin resins and the first occurring delamination. However, it is very likely that the progress of specimen delamination is not in a continuous and smooth fashion but rather than in an abrupt and irregular way. The load went to high levels before the sudden debond, at which the force subsequently dropped down and increased again until the next delamination; at the last peak, the specimen was flexible enough not to carry out any load. This delamination behavior indicates the poor wettability probably caused by the lack of tannin resins, which did not impregnate completely within the eight fibre plies. Another reason is the poor flax/tannin adhesion caused by the incompatibility between flax (hydrophilic) and tannin resins (hydrophobic).

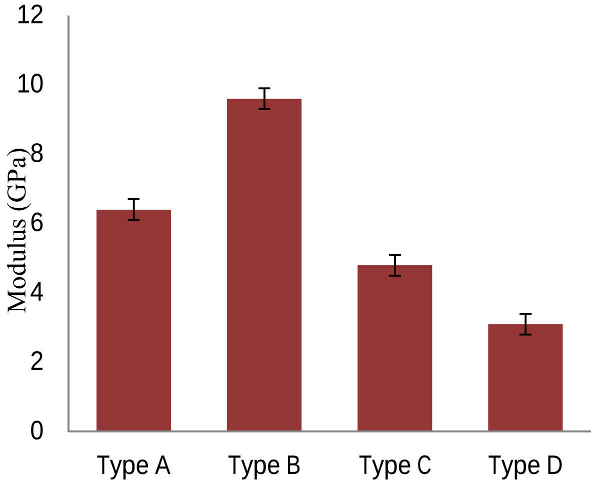

Figure 3. Tensile modulus of various flax/tannin composites.

3.2. Scanning electron microscopy

SEM micrographs for tensile surfaces of flax/tannin composites with various lay-up angles are shown in **Figure 4** and **Figure 5**. As discussed previously, composites B, C and D showed delamination behaviour without fracture during tensile testing and one of the delaminated samples were then cut into specimen and investigated by SEM. **Figure 4** (a) clearly shows the separation of fibre layers upon testing, indicating the poor surface adhesion between these fabric layers. Some noticeable gaps between matrix and fibres are indicated by 'A' which represents the non-contact fibre/matrix surface attributable to the fibre debonding and weak performances. It is advised to utilize chemical treatment like alkali treatment to enhance the fibre/matrix interfacial adhesion by purifying the fibre surface and improving the possibility for chemical bonding [20]. Also, an advanced approach for the problems is nano-scale fibres leading to remarkable fibre dispersion, hence good intermolecular interactions.

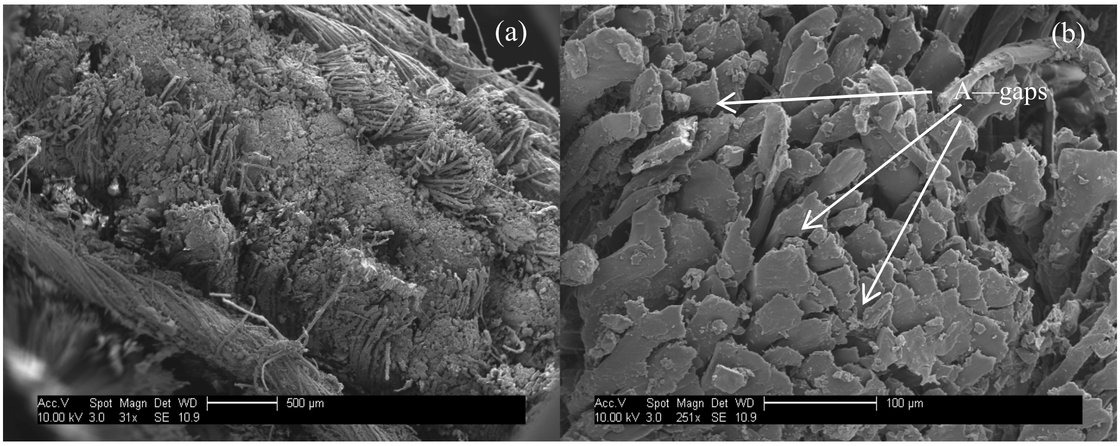

Figure 4. SEM micrographs of a cut non-fractured sample.

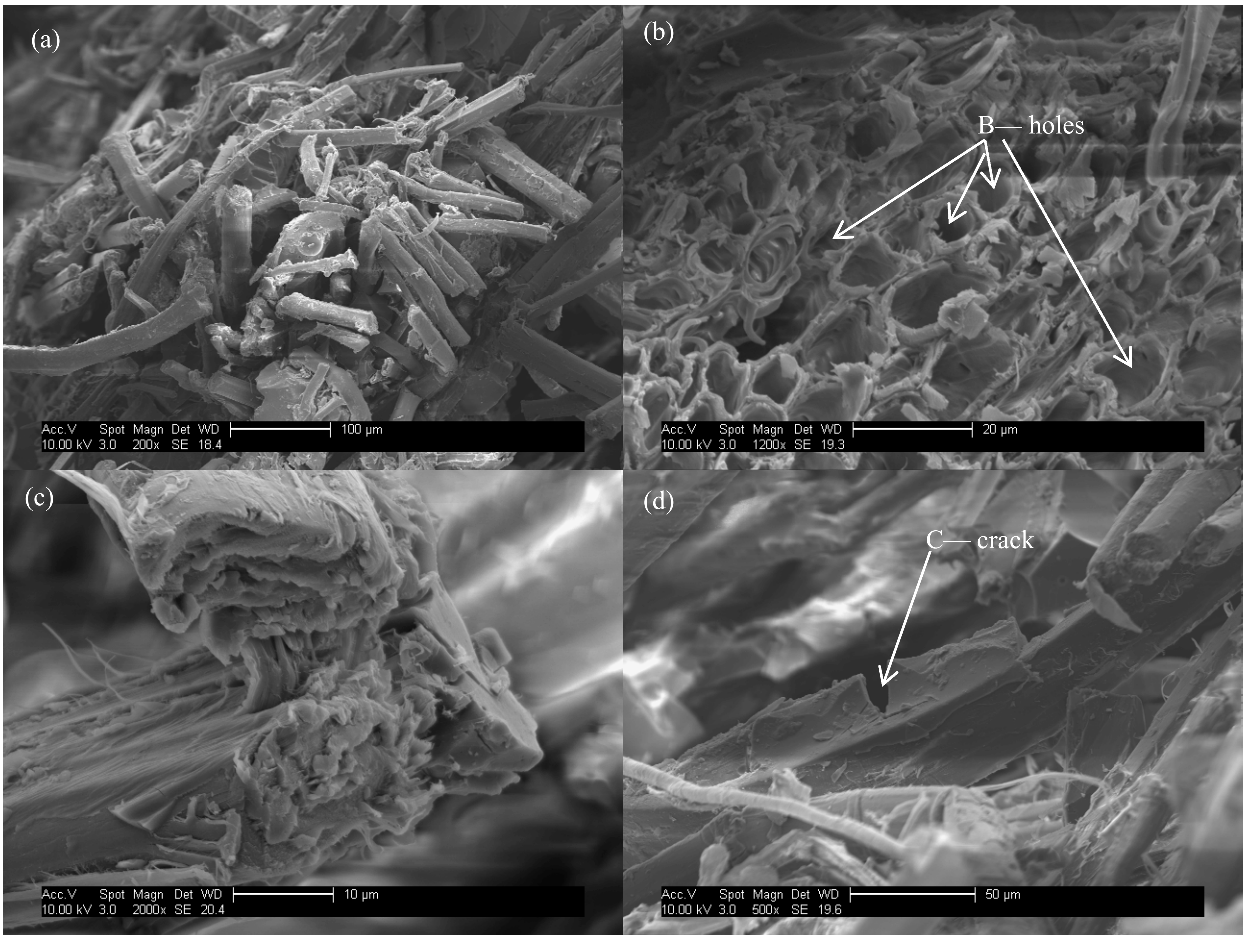

Figure 5. SEM micrographs of tensile fractured flax mat reinforced composites (Type A).

Figure 5 is the cross-sectional micrographs of tensile fracture surface. The failure mechanism shown in the figure is complicated. According to **Figure 5**(a), the bonding quality between fibre layers is fairly better than that of non-fracture specimen. **Figure 5**(b) shows the remaining holes (indicated by 'B') after fibre pull-out. The fibre breakage shown in **Error! Reference source not found.**(c) is caused by the applied stress. Symbol 'C' in **Figure 5**(d) points to a small crack within the tannin resins adjacent to fibres. This is brittle failure of tannin resins under tension force. Based on the investigations, the failure of flax fibre reinforced tannin matrix composites (ENSTIB) is governed by the combination of fibre pull-out, fibre fracture and brittle fracture of tannin resins.

4. Conclusions

Supported by ECHOSHELL project, flax/tannin composites with various fibre fabric orientations were supplied by the MaHyTec and ENSTIB. These composites were prepared by sheet compression moulding (SMC), and received by Cranfield University for further characterisation and modification. Tensile tests using DIC method and subsequent SEM characterisation on the composites were shown in the conference paper. It is apparently that the UD flax-reinforced tannin-based composites show the highest tensile strength of up to 150 MPa and elastic modulus of 9.6 MPa, as a result of longitudinal reinforcement. The trend in tensile strength partially depends on the numbers of UD oriented flax mat in the composites. The 'z' curves after failure in the load-extension figure suggest the discontinuous delamination progress probably originated from the in-sufficient wettability between flax fibres and tannin resins. SEM characterisation revealed the interface adhesion in the delaminated samples and also showed failure mechanisms (fibre pull-out, fibre breakage and brittle tannin failure) of the tensile fractured samples. These results are very competitive to the literature findings and show a good mechanical performance potential with further surface treatment (e.g. alkali treatment) or use of nano-scale flax fibres from adequate techniques (e.g. high pressure disintegration).

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